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### OFFICE OF NAVAL RESEARCH

### **END-OF-THE-YEAR REPORT**

### PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT or CONTRACT: N00014-98-1-0499

PR NUMBER: 98PR05110-00

"Nanowire Thermoelectrics: An Approach for Enhancing ZT"

Charles M. Lieber Principal Investigator

Harvard University

Department of Chemistry and Chemical Biology 12 Oxford Street Cambridge, Massachusetts 02138

> Date Submitted: June 29, 1998

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### OFFICE OF NAVAL RESEARCH PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

PR Number: 98PR05110-00

Contract/Grant Number: N00014-98-1-0499

Contract/Grant Title: "Nanowire Thermoelectrics: An Approach for Enhancing ZT"

Principal Investigator: Charles M. Lieber Mailing Address: Harvard University

Department of Chemistry and Chemical Biology 12 Oxford Street, Cambridge, Massachusetts 02138

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a. • Number of papers submitted to refereed journals, but not published: 0

b. • Number of papers published in refereed journals (for each, provide a complete citation): 0

c. • Number of books or chapters submitted, but not yet published: 0

- d. Number of books or chapters published (for each, provide a complete citation): 0
- Number of printed technical reports/non-refereed papers (for each, provide a complete citation: 0

f. • Number of patents filed: 0

- Number of patents granted (for each, provide a complete citation): 0
- h. Number of invited presentations (for each, provide a complete citation): 6
  i. Number of submitted presentations (for each, provide a complete citation): 0

• Honors/Awards/Prizes for contract/grant employees (list attached): 2

k. • Total number of Full-time Equivalent Graduate Students and Post-Doctoral associates supported during this period under PR project number: 1

Graduate Students: 1

Post-Doctoral Associates: 0

including the number of:

Female Graduate Students: 0

Female Post-Doctoral Associates: 0

the number of

Minority Graduate Students: 0

Minority Post-Doctoral Associates: 0

and the number of

Asian Graduate Students: 0

Asian Post-Doctoral Associates: 0

- 1. Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant).
  - Use the letter and an appropriate title as a heading for your list, e.g.:
- b. Published Papers in Refereed Journals, or, d. Books and Chapters published. Also submit the citation lists as ASCII files via email or via PC-compatible floppy disks.
- Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

- h. Number of invited presentations: 6
  - 1. "Chemistry and Physics in 1D: Growth, Properties and Applications of Nanowires and Nanotubes", University of California at Los Angeles, Los Angeles, CA, April 1998.
  - 2. "Buckytubes: New Toys (and More) for Physics and Chemistry", Princeton University, Princeton, NJ, April 1998.
  - 3. "One-Dimensional Nanostructures: Novel Properties of Nanotubes and Nanowires", Department of Physics, University of California at Berkeley, Berkeley, CA, April 1998.
  - 4. "Chemistry and Physics in 1D", Department of Chemistry, University of California at Berkeley, Berkeley, CA, April 1998.
  - 5. "Nanotubes", 1998 JASON Spring Meeting, The Mitre Corporation, McLean, VA, April 1998.
  - 6. "Chemistry and Physics in 1D: Synthesis, Properties and Applications of Nanostructures", Materials for the 21st Century and Beyond, 12th Annual Symposium of the Center for Study of Gene Structure and Function, Hunter College, New York, NY, April 1998.
- j. Honors/Awards/Prizes for contract/grant employees: 2
  - 1. Editorial Advisory Board, Advanced Materials, elected 1998.
  - 2. Associate Member, International Union of Pure and Applied Chemistry, elected 1998.
- 1. Other funding:

A. Agency: National Science Foundation

Grant Title: "Scanning Tunneling Microscopy Investigations

of Low-Dimensional Materials."

Amount to be received this year: \$150,000

Total Amount: \$300,000

Period of Performance: 8/15/96 - 8/14/98

This grant has no direct overlap with the work of this ONR project.

B. Agency: Air Force Office of Scientific Research

Grant Title: "Nanotribology Investigations of Solid and Liquid Lubricants

Using Scanned Probe Microscopies." Amount received this year: \$275,000

Total Amount: \$575,000

Period of Performance: 11/1/96 - 10/31/99

This grant has no direct overlap with the work of this ONR project.

C. Agency: Air Force Office of Scientific Research

Grant Title: "Nanometric Studies of the Structure and Tribology of Carbon

Nitride Materials."

Amount received this year: \$55,972

Total Amount: \$167,953

Period of Performance: 6/15/95 - 6/14/98

This grant has no direct overlap with the work of this ONR project.

D. Agency: Ballistic Missile Defense Organization

Grant Title: "Spectroscopic Characterization of Laser Ablation Plumes for

Advanced Materials Growth."

Amount received this year: \$150,900

Total Amount: \$150,900

Period of Performance: 3/1/97 - 2/28/98

This grant has no direct overlap with the work of this ONR project.

E. Agency: National Science Foundation (Materials Research Science and

**Engineering Center**)

Grant Title: "Long-Range Order and Winding of Vortices in High-T<sub>c</sub>

Superconductors"

P.I.s: D.R. Nelson and C.M. Lieber Amount received this year: \$50,000

Total Amount: \$50,000

Period of Performance: 3/1/97 - 2/28/98

This grant has no direct overlap with the work of this ONR project.

F. Agency: National Science Foundation (Materials Research Science and

Engineering Center)

Grant Title: "Synthesis of Superhard Carbon Nitride Materials"

P.I.s: C.B. Agee, M.J. Aziz and C.M. Lieber

Amount received this year: \$50,000 Period of Performance: 3/1/97 - 2/28/98

This grant has no direct overlap with the work of this ONR project.

G. Agency: American Chemical Society - The Petroleum Research Fund

Grant Title: "Growth of 1-Dimensional Carbide Nanomaterials."

Amount received this year: \$25,000

Total Amount: \$50,000

Period of Performance: 1/1/97 - 8/31/99

This grant has no direct overlap with the work of this ONR project.

H. Agency: National Institutes of Health (subcontract from Brigham &

Women's Hospital)

Grant Title: "Analysis of Alzheimer Amyloidogenesis with New Methods"

Amount received this year: \$109,421

Total Amount: \$109,421

Period of Performance: 6/1/97-5/30/98

This grant has no direct overlap with the work of this ONR project.

### **PART II**

a. Principle Investigator: Charles M. Lieber

b. Current telephone number: (617) 496-3169

c. Cognizant ONR Scientific Officer: Dr. John C. Pazik

### d. Program objective:

The overall objectives of the AASERT project are to develop an approach for the controlled synthesis of single crystal, one-dimensional (1D) nanowires of the Bi<sub>2</sub>Te<sub>3</sub> family of thermoelectric materials, and to characterize the potentially unique electronic properties of these 1D systems. To achieve these goals we will (1) develop synthetic procedures, which were initiated as part of our current ONR project on nanorod-superconductor composites, to prepare Bi<sub>2</sub>Te<sub>3</sub> nanowires and (2) exploit existing scanning tunneling microscopy facilities and expertise to characterize the nanowire density of electronic states. The combination of systematic synthesis with high-resolution structural and electronic characterization will elucidate the basic factors that control the diameter, aspect ratio, and crystallographic growth direction of Bi<sub>2</sub>Te<sub>3</sub> nanowires, and define the variation and potential enhancements in valence and conduction band edge density of states with nanowire diameter. These studies will thus provide a critical assessment of the possiblity of obtaining enhanced thermoelectric figures of merit through material dimensional control.

### e. Significant results during last year:

Several significant results have been obtained during the first few months since this program was initiated. We have developed and tested a general approach for the growth of nanowires of a wide range of interesting materials. In this method, a pulsed laser is used to vaporize a target consisting of the compound of interest (e.g.,  $\mathrm{Bi}_2\mathrm{Te}_3$ ) and a small percentage of catalyst. As the atomic vapor of the compound and catalyst cools to the equilibrium temperature of the reactor, clustering occurs to yield a moltent alloy of the catalyst and reactants. When the liquid catalyst alloy becomes supersaturated with excess compound, nucleation followed by 1D nanowire growth occurs . We have verified the overall features and generality of this synthetic approach in studies of Si and Ge, where we produced single crystal Si and Ge nanowires with diameters between 3 and 20 nm and lengths in excess of 1 µm. Recently, we have applied this new approach to the rational growth of  $\mathrm{Bi}_2\mathrm{Te}_3$  using a gold catalyst, and significantly, preliminary results indicate that crystalline  $\mathrm{Bi}_2\mathrm{Te}_3$  nanowires have been obtained.

f. Brief summary of plans for next years work:

The major goals of this project for the coming year will be (1) to develop further our synthesis of  $Bi_2Te_3$  nanowires, (2) to define the relationship between growth conditions and nanowire size and structural properties, and (3) to exploit existing scanning tunneling microscopy facilities to characterize the nanowire density of electronic states.

- g. List of names of graduate students and post-doctoral(s) currently working on project:
  - 1. Paul Ashby

Principle Investigator: Charles M. Lieber

Project Title: "Nanowire Thermoelectrics: An Approach for Enhancing ZT"

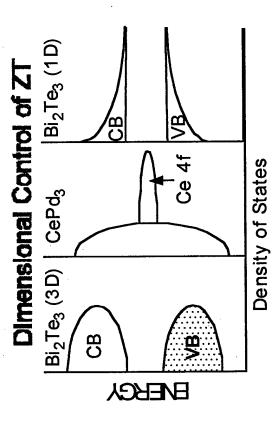
Cognizant ONR Scientific Officer: Dr. John C. Pazik

Highlights of Research Project: 4/98 to 6/98

### Nanowire Thermoelectrics

**Technology Issues:** improved thermoelectric figure of merit, ZT, is critical to Navy and commercial applications

Objectives: develop general approach for growth of crystalline thermoelectric quantum wires; characterize nanowire density of electronic states



### Approach:

- use nanocluster catalyst to define size of nanowire during growth
- use laser ablation to control size of clusters and generate reactants
- use STM to elucidate novel electronic properties

Accomplishments:

Impact

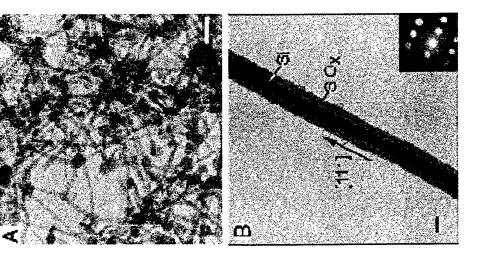
- general approach for nanowire growth developed and demonstrated with growth of Si nanowires
- method extended to binary compounds; bulk GaAs quantum wires produced
- new and general approach to prepare materials with controlled dimensionality
- promise of improved ZT in Bi<sub>2</sub>Te<sub>3</sub> system
- applications to 3D computing

## General Approach For Nanowire Growth

• Growth Scheme

Furnace reactant

• Proof-of-Concept: Si Nanowires



# Growth of Binary Semiconductor Nanowires

Ternary Phase Diagram
 Defines Catalyst and
 Growth Conditions

